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Gas phase clustering of N2 molecules on to TiO+: Comparison with Ti+ and evidence for the octahedral structure of TiO+(N2)5

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Gas phase clustering of N_2 molecules on to TiO^+: Comparison with Ti^+ and evidence for the octahedral structure of $TiO^+(N_2)_5$

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In recent years considerable experimental and theoretical effort has been devoted to studies of metal ion-doped molecular clusters in order to provide a better understanding of the many-body interactions between a metal ion and neutral molecules. Most of the work in this area has focused on measuring thermochemical quantities (sequential bond enthalpies and entropies) for the clustering of rare gas atoms and simple molecules with alkali metal ions,[1,2] laser spectroscopy of ion clusters in molecular beams[3,4] and extensive theoretical work on the structures and binding energies of these systems.[5] Recent studies have involved clusters containing transition metal ions, and several interesting features have been observed and interpreted in terms of the electronic structure of the transition metal cationic center.[6] However, very little work has been directed toward the clustering of neutral molecules onto metal oxide cationic centers. It appears, therefore, that there is a need for further work in this direction.

In the course of some recent experiments involving gas phase reactions of Ti^+ with isobutylene under variable pressures,[7] we had the need to study the reactions of Ti^+ with different carrier gases such as He, Ar, and N_2. As these gases usually contain small amounts of O_2, both Ti^+ and TiO^+ were observed under different conditions of carrier gas pressure and temperature. It seemed of some interest to compare the clustering reactions of a simple diatomic molecule such as N_2 onto Ti^+ and TiO^+ ions. Such a comparison is the purpose of this Note. There are two specific points of particular interest in the present study. The first is the effect the presence of oxygen has on the clustering efficiency of Ti^+ with N_2 molecules. The second point is whether a solvent shell or a stable coordination structure would be observed around TiO^+.

The experiments follow the pulsed laser vaporization high pressure mass spectrometry (LVHPMS) methodology.[7,8] The Ti^+ ions are generated by laser vaporization of a titanium rod using the second harmonic of a Nd:YAG laser (532 nm, energy <10 mJ/pulse) pulsed at 20 Hz. The ions are produced inside a temperature controlled, high pressure source. The pressure is measured with a Baratron capacitance manometer coupled with the gas inlet tube. Ions exit the source through a 0.02 cm diam hole. The quadrupole mass filter (Extrel C-50) is mounted coaxially to the ion exit hole. The operating pressure in the mass spectrometer region is typically $1\text{–}8\times10^{-6}$ torr. The titanium rod was obtained from Aldrich with a stated purity of 99.97%.

TiO^+ ions are observed to form readily in the ion source in the presence of a carrier gas (He, Ar, or N_2) containing a trace amount of O_2 (less than 0.05%). O_2 is known to efficiently oxidize Ti^+ in the gas phase[9] due to the very high bond strength of the Ti^+–O bond (161 kcal/mol).[10] Therefore, the propensity of Ti^+ to undergo oxidation in the presence of a very low concentration of O_2 is not surprising. Figures 1(a)–(c) display typical mass spectra observed at different source pressures of Ar at room temperature. It is clear that the intensity ratio of the ions TiO^+/Ti^+ increases rapidly with increasing the pressure in the ion source. Similar observations are found for He and N_2. Figure 2 exhibits the mass spectrum observed at a total N_2 pressure of 0.19 torr and a source temperature in the range of 100–110 K. The results indicate a striking difference in the clustering of N_2 molecules onto Ti^+ and TiO^+. The only peaks in the mass spectrum shown in Fig. 2 are due to the cluster ions $TiO^+(N_2)_n$ and $TiO^+(O_2)_m(N_2)_n$ with $m+n\leqslant5$ and no such clustering is observed for Ti^+. This would appear to indicate that the $TiO^+(N_2)_n$ clusters are more stable than the analogous sequence for Ti^+. Another intriguing feature of the $TiO^+(N_2)_n$ series is the strong magic number observed for the $n=5$ cluster. We note that the ion intensity ratio for $(n=5)/(n=4)$ is greater than 3.5 while that for $(n=6)/(n=5)$ is essentially zero. Interestingly, further increase in the pressure of N_2 does not cause any more clustering of N_2 molecules

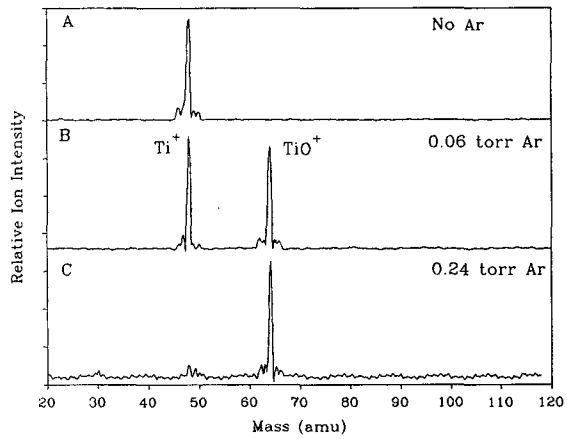

FIG. 1. (A) Mass spectrum of Ti^+ produced by laser vaporization in the absence of any carrier gas at room temperature, pressure $=1\times10^{-7}$ torr; (B) in presence of 0.06 torr of Ar; (C) 0.24 torr of Ar.

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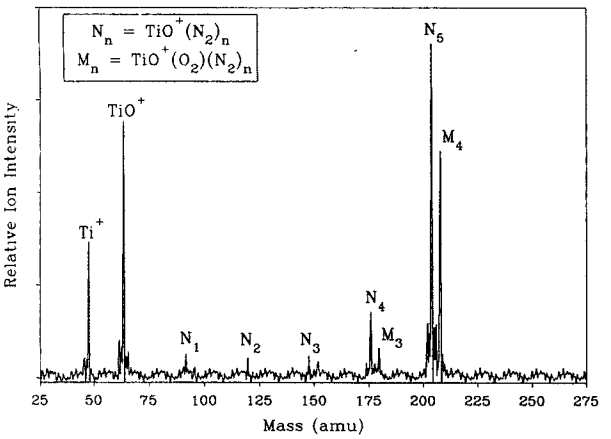


FIG. 2. Mass spectrum of $TiO^+(N_2)_n$ and $TiO^+(O_2)_m(N_2)_n$ at 0.19 torr of N_2 and $T=100$–110 K.

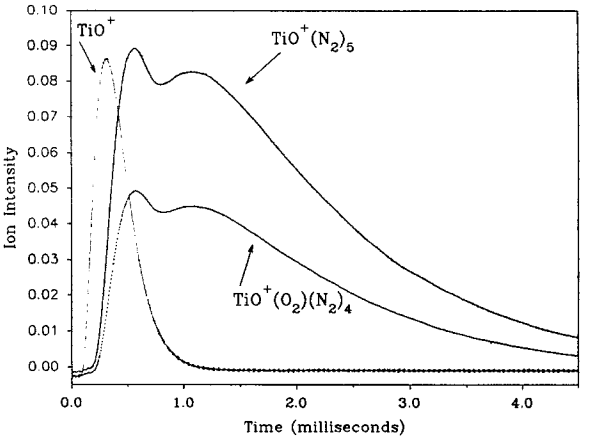
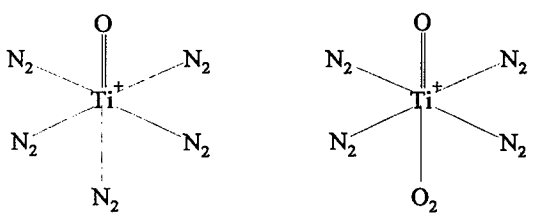


FIG. 3. Temporal profiles of TiO^+, $TiO^+(N_2)_5$, and $TiO^+(O_2)(N_2)_4$ at a source pressure of 0.19 torr and a temperature of 100–110 K.

onto $TiO^+(N_2)_5$. This suggests that only five N_2 molecules are required to block all the available bonding sites on TiO^+. Further N_2 molecules past $n=5$ would attach to the $TiO^+(N_2)_5$ with very weak forces and therefore are not observed under the thermal conditions achieved in the present experiment. The same blocking effect is also observed for the cluster $TiO^+(O_2)(N_2)_4$ and no further additions of O_2 or N_2 molecules could be observed. The structures proposed for these magic number clusters can be pictured as simple octahedral structures as shown below.



It is worth noting that Guo and Castleman have recently observed efficient clustering of three ethylene molecules onto TiO^+ and no more ethylene molecules could be attached to the $TiO^+(C_2H_4)_3$ cluster even at higher source pressures.[11] This indicates that both tetrahedral and octahedral clusters can be formed with TiO^+ as a core ion.

The efficient clustering of TiO^+ can be explained in terms of the electron withdrawing ability of the oxygen atom which can result in an electronic structure of TiO^+ that might be described as $Ti^{3+}O^{2-}$. This interpretation is consistent with the common octahedral structures observed for the coordination complexes of Ti^{3+} in solution[12] such as $[Ti(H_2O)_6]^{3+}$ and $[TiF_6]^{3-}$. Figure 3 displays the temporal profiles of the ions TiO^+, $TiO^+(N_2)_5$, and $TiO^+(O_2)(N_2)_4$. From this data it is evident that the decay rate of the TiO^+ ions is very fast (i.e., collision rate) while those of the filled structures [$TiO^+(N_2)_5$ and $TiO^+(O_2)(N_2)_4$] are very slow. This behavior provides further evidence for the unfavorable clustering of N_2 molecules past $n=5$. The data also suggests that a ligand exchange reaction can take place within the stable sequence of $TiO^+(O_2)_m(N_2)_n$, $(m+n=5)$ according to

$$TiO^+(N_2)_5+O_2 \rightleftharpoons TiO^+(O_2)(N_2)_4+N_2.$$

In conclusion, we have observed a striking difference in the clustering efficiency of Ti^+ and TiO^+ and obtained strong evidence for the magic number $n=5$ within the sequence $TiO^+(N_2)_n$. These results are consistent with an octahedral structure for $TiO^+(N_2)_5$.

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[1] P. Kebarle, Annu. Rev. Phys. Chem. **28**, 445 (1977).
[2] R. G. Keesee and A. W. Castleman, Jr., J. Phys. Chem. Ref. Data **15**, 1011 (1986).
[3] M. H. Shen and J. M. Farrar, J. Phys. Chem. **93**, 4386 (1989).
[4] T. J. Selegue, N. Moe, J. A. Draves, and J. M. Lisy, J. Chem. Phys. **96**, 7268 (1992).
[5] H. Partridge, C. W. Bauschlicher, and S. R. Langhoff, J. Phys. Chem. **96**, 5350 (1992).
[6] P. R. Kemper, M. T. Hsu, and M. T. Bowers, J. Chem. Phys. **96**, 5350 (1992).
[7] G. M. Daly and M. S. El-Shall, J. Phys. Chem. (submitted, 1993).
[8] M. S. El-Shall, K. E. Schriver, R. L. Whetten, and M. Meot-Ner (Mautner), J. Phys. Chem. **93**, 7969 (1989).
[9] D. L. Hildebrand, Chem. Phys. Lett. **44**, 281 (1976).
[10] M. M. Kappes and R. H. Staley, J. Phys. Chem. **85**, 942 (1981).
[11] B. C. Guo and A. W. Castleman, Jr., J. Am. Chem. Soc. **114**, 6152 (1992).
[12] H. L. Schlafer and G. Glieman, *Basic Principles of Ligand Field Theory* (Wiley, New York, 1969).